Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere

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Streams, rivers, lakes, and other inland waters are important agents in the coupling of biogeochemical cycles between continents, atmosphere, and oceans. The depiction of these roles in global-scale assessments of carbon (C) and other bioactive elements remains limited, yet recent findings suggest that C discharged to the oceans is only a fraction of that entering rivers from terrestrial ecosystems via soil respiration, leaching, chemical weathering, and physical erosion. Most of this C influx is returned to the atmosphere from inland waters as carbon dioxide (CO_2) or buried in sedimentary deposits within impoundments, lakes, floodplains, and other wetlands. Carbon and mineral cycles are coupled by both erosion–deposition processes and chemical weathering, with the latter producing dissolved inorganic C and carbonate buffering capacity that strongly modulate downstream pH, biological production of calcium-carbonate shells, and CO_2 outgassing in rivers, estuaries, and coastal zones. Human activities substantially affect all of these processes.

Rivers and other inland water systems represent distinct ecosystems, geomorphological agents, sites of biogeochemical storage and transformation, and conduits for material transport across continents and to the oceans, and are linked with human health and economic activity (Figures 1 and 2). Although the importance of rivers in modulating the transfer of nutrients from the land to coastal areas has long been recognized (Smith and Hollibaugh 1993), rivers are typically considered as passive "pipes" in regional and global budgets of carbon (C) and weathering products (ie dissolved ions and sediment). Recent studies and syntheses have overturned this view of rivers as passive transporters (Richey *et al.* 2002; Cole *et al.* 2007; Battin *et al.* 2009; Tranvik *et al.* 2009) and of weathering exports as unresponsive to human impacts (Raymond *et al.* 2008). A key finding is that the amount of C that rivers deliver to the oceans is only a fraction of that entering rivers from terrestrial ecosystems (Figure 3). Most of this C is returned to the atmosphere in the form of carbon dioxide (CO_2) before reaching the oceans or is stored within river corridors as sedimentary organic carbon (OC) after erosion and transport from distant sites. Understanding the interplay between reactivity, transport, and coupling among landscape components (ie uplands, riparian zones, streams and rivers, wetlands, lakes, floodplains) is a fundamental challenge for characterizing the susceptibility of riverine biogeochemical function to climate and land-use change.
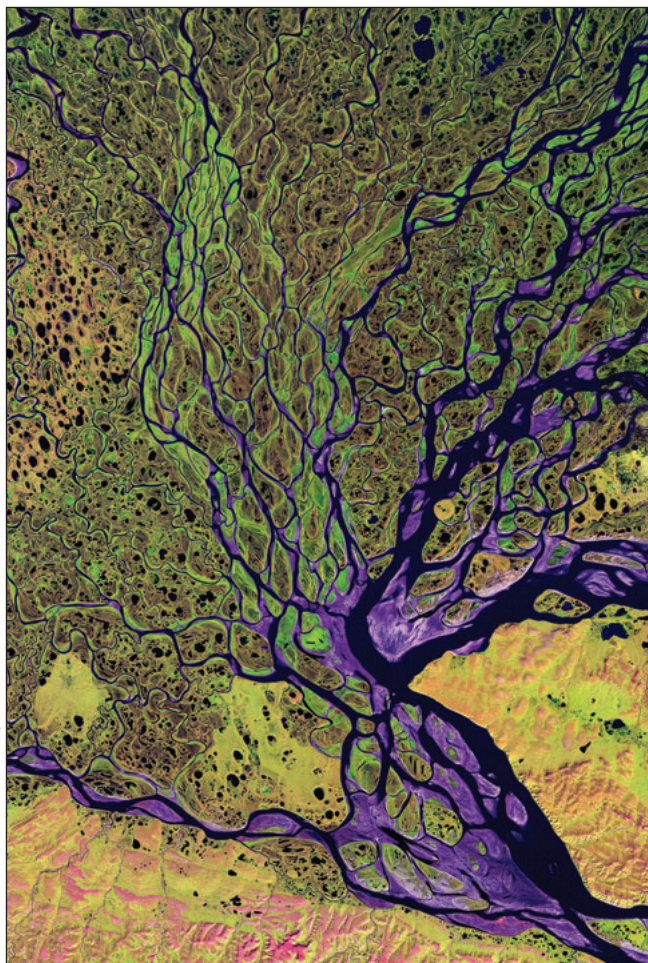
Here we concentrate on three important aspects of water, C, and mineral cycles – linked together – to illustrate the role of rivers and other inland waters as biogeochemical couplers of landscapes and Earth-system components (ie continents, oceans, atmosphere):

(1) The lateral exports of C from terrestrial ecosystems by streams and subsequent CO_2 outgassing to the atmosphere, highlighting their increasingly recognized importance for closing terrestrial net ecosystem C balance (see Panel 1);

(2) The erosion, mixing, and burial of minerals and associated OC, including the coupling of C sequestration with geomorphological drivers;

(3) The influence of river exports of alkalinity and major ions on coastal responses to ocean acidification, including the effects of human perturbation within watersheds on mineral weathering.
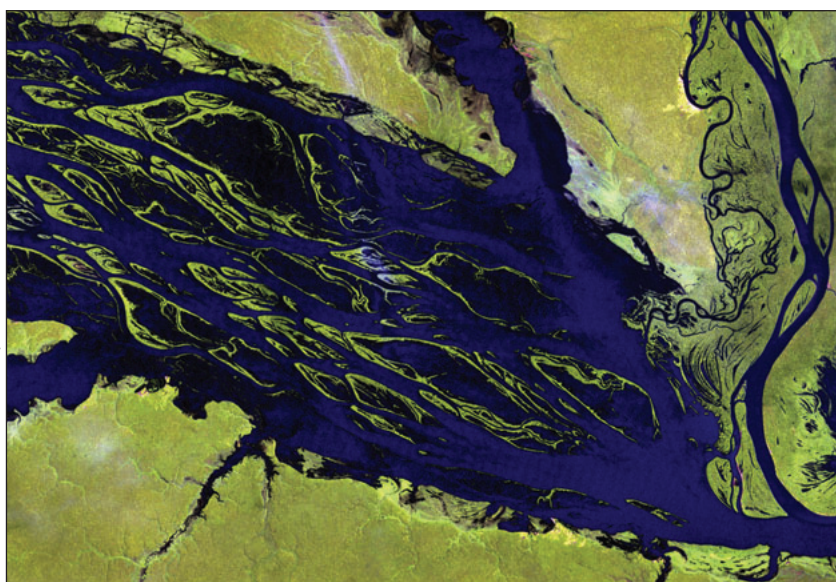
In a nutshell:

- Rivers and other inland waters receive, transport, process, and return to the atmosphere amounts of carbon (C) of similar magnitude to the net ecosystem C balance of the terrestrial ecosystems in their watersheds
- Burial of C on continents – within sedimentary deposits of inland waters – is an order of magnitude greater than burial of C in the oceans
- Human-accelerated chemical weathering of minerals in watersheds affects coastal-zone acidification

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N

Figure 1. The delta of Russia's Lena River. Terrestrial and aquatic ecosystems closely intermingle in many continental areas across the world, such as boreal ecosystems.

ments (ie C, nitrogen [N], phosphorus [P], oxygen [O], and sulfur [S]), which we assume to be implicit in our discussion of C processing. Also, we consider most inland waters – such as streams, lakes, impoundments, and the many types of wetlands – as being components of river systems. Although each of these inland water types represents a distinct ecosystem with associated processes, nearly all receive and/or discharge materials from/to the river networks to which they are coupled.

■ From land to river to atmosphere: C under the radar

In the early 1990s, a decade's worth of oceanographic and global C modeling identified a significant "missing carbon sink" on continents that was equivalent to about one-third of global fossil-fuel emissions, launching numerous research efforts to quantify the net storage of C in the major terrestrial ecosystems. Nearly two decades later, a consensus has yet to emerge regarding the spatial distribution of terrestrial C sinks. One roadblock is that net ecosystem production (NEP) measured at local scales does not often extrapolate well to larger scales (Ometto *et al.* 2005; Stephens *et al.* 2007). These discrepancies may be due to the assumption that all NEP is converted entirely to storage, without consideration of lateral export (Panel 1). Recent findings suggest that, in many cases, lateral exports – through rivers, airborne transport of reduced C compounds, and commercial trade in food and forest products – can be of equal magnitude to storage fluxes (Richey *et al.* 2002; Billett *et al.* 2004; Ciais *et al.* 2008). This observation may help reconcile disparate estimates of C sequestration and provide improved estimates of terrestrial NEP (Billett *et al.* 2004; Cole *et al.* 2007).

Our consideration of coupling focuses primarily on that between continents, oceans, and atmosphere by rivers and other inland waters. We mainly consider biogeochemical coupling between C and inorganic species, such as alumino-silicate and carbonate minerals, in the context of geochemical and geomorphological processes, rather than coupling between different bioactive ele-

Aquatic biogeochemists have established that nearly all fresh waters contain CO_2 in concentrations that are supersaturated with respect to that of the atmosphere. The partial pressure of dissolved CO_2 (pCO_2; Panel 2) in water in equilibrium with the atmosphere is equivalent to the concentration of CO_2 in the atmosphere, which is currently about 390 parts per million (ppm) by volume. Measured pCO_2 values typically range from 1000 to more than 12 000 ppm in rivers (Cole and Caraco 2001; Richey *et al.* 2002; Johnson *et al.* 2008; Humborg *et al.* 2010) and from 350

Figure 2. The Negro River in the central Amazon, just upstream of the confluence with the Branco River. River floodplains and inland waters are dynamic systems that link Earth systems across large spatial and temporal scales.

C

Carbon

12.011

to more than 10 000 ppm in lakes and reservoirs (Sobek *et al.* 2005; Marotta *et al.* 2009) – with tropical waters typically exhibiting higher concentrations of CO_2 than temperate waters, and rivers and wetlands typically having higher concentrations of CO_2 than lakes (Table 1). These values show large net freshwater-to-atmosphere CO_2 fluxes, which must be balanced by substantial inputs from terrestrial systems, as either OC or CO_2-rich groundwater (Mayorga *et al.* 2005; Johnson *et al.* 2008). The translation of water–air CO_2 gradients to areal fluxes requires multiplication by gas exchange velocities (k), which vary as a function of turbulence in the surface water and, to a lesser degree, with temperature (Table 1 and WebPanel 1). The CO_2 fluxes from one square meter of surface water can therefore be much higher than CO_2 fluxes into one square meter of the adjacent terrestrial ecosystem (Table 1).

Regional and global estimates of CO_2 outgassing fluxes rely as much on estimates of inland water area as on the CO_2 fluxes per unit area of surface water. Over the past few years, our estimation of inland water area has substantially increased as a result of (1) improvements in remote-sensing approaches, often combining data captured from multiple airborne- and satellite-borne sensors to assess flooding beneath vegetation (Hess *et al.* 2003; Prigent *et al.* 2007), and (2) compilations and algorithms to estimate areal coverage of water bodies (Lehner and Döll 2004; Downing 2009). Recent studies have more than doubled the global land area known to be seasonally to permanently inundated to over 20 million km^2 (Lehner and Döll 2004; Downing 2009), an area roughly equivalent to 15% of global land surfaces, excluding Antarctica and Greenland (Table 1). These improved estimates of inundated area translate to proportional increases in the magni-
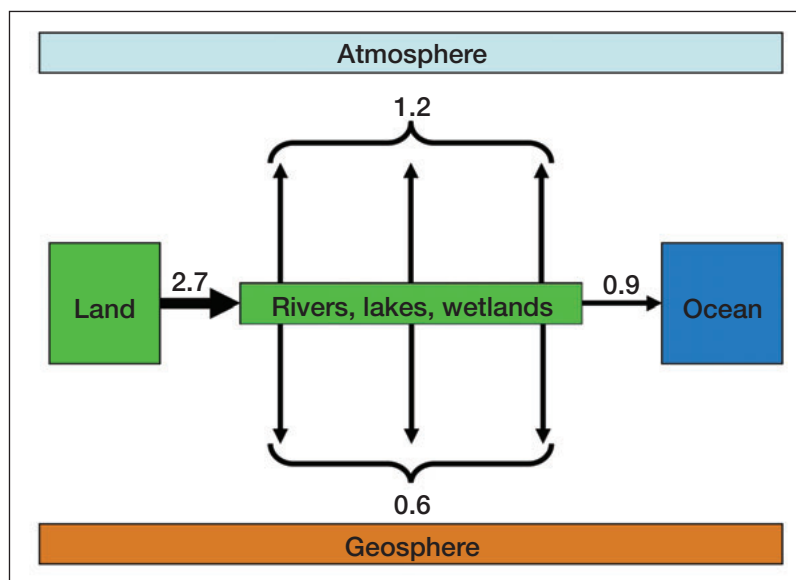
Figure 3. *The coupling of land, oceans, and atmosphere by rivers, lakes, and wetlands. All numbers are fluxes in units of Pg C yr^{-1}, with values based on an analysis by Battin et al. (2009); accumulation fluxes within both land and ocean each equal 2.2 Pg C yr^{-1}. The CO_2 outgassing and continental burial fluxes from Battin et al. (2009) are substantially larger than those published by Cole et al. (2007), primarily on account of more complete consideration of high-latitude lakes. A more balanced inclusion of tropical waters and wetlands, and temperature dependencies on pCO$_2$ and k, as we consider in Table 1, would require a further increase in outgassing fluxes to the atmosphere. These flux values have direct consequences to net C balances on land because of the need to balance the global C budget.*

tudes of outgassing fluxes.

Published estimates of the global flux of CO_2 outgassing from inland surface waters range from 0.75 to 1.4 petagrams of C per year (Pg C yr^{-1}; Figure 3), which is globally important when compared with estimates of net C accumulation on continents (2.2 Pg C yr^{-1}) or in the oceans (2.2 Pg C yr^{-1}; Cole and Caraco 2001; Cole *et al.* 2007; Battin *et al.* 2009; Takahashi *et al.* 2009; Tranvik *et al.* 2009). Yet these CO_2 fluxes from inland waters directly to the atmosphere are rarely considered in global or regional

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Panel 1. Terms of terrestrial ecosystem carbon budgeting

Net ecosystem production (NEP) is the difference between gross primary production and the community respiration of an ecosystem, typically reported in units of C per unit time per unit area. NEP represents the amount of C available for storage or export over a given time interval, with a positive value for net autotrophic ecosystems and a negative value for net heterotrophic ecosystems. Although a fundamental property of an ecosystem, NEP is challenging to measure over annual and decadal time scales. The historical approach for terrestrial ecosystems has been to measure changes in C stocks in biomass and soils over many years, with the implicit assumption that lateral C export is negligible. A more recent approach has been to deploy sensors for CO_2 and wind on a tower – emerging from the forest canopy – to take measurements of the turbulent vertical fluxes of CO_2 every few seconds for a period of years. Data from these "eddy covariance flux" towers are integrated to quantify the net amount of CO_2 transported into the forest from the atmosphere, which is known as net ecosystem exchange (NEE, where NEE < 0 represents a land sink for CO_2). The assumption has been that lateral export is negligible and that NEE equals NEP, but several new studies have called into question these assumptions and assert that lateral export of C from terrestrial ecosystems – via rivers and other processes – may be substantial relative to NEP or NEE (Richey *et al.* 2002; Billett *et al.* 2004; Cole *et al.* 2007; Ciais *et al.* 2008). As a result, an effort has been made to remind the terrestrial ecosystem research community of the original definition of NEP, which includes export (Lovett *et al.* 2006), and to introduce a less ambiguous term, net ecosystem carbon balance (NECB), to describe only the flux of C available for local storage (Chapin *et al.* 2006).

P

Phosphorus

30.974

Panel 2. Dissolved carbon dioxide, explained

Dissolved carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}) are collectively referred to as dissolved inorganic carbon (DIC). These chemical species readily interconvert from one to another as a function of their relative concentrations, pH, temperature, and the concentrations of other buffering and complexing species. With a gas species (CO_2) at one end of the reaction chain and several mineral species at the other (eg calcium carbonate, $CaCO_3$), the carbonate buffering system – as this series of related reactions is known – can only be understood by simultaneously solving a series of thermodynamic equations. The carbonate buffering system is further coupled to mineral cycles because carbonate alkalinity ($Carb_{alk} = [HCO_3^-] + 2 \times [CO_3^{2-}]$) is controlled by the thermodynamic requirement to balance the electrostatic charge imbalance between strong base cations (eg calcium [Ca^{2+}], manganese [Mg^{2+}], sodium [Na^+], potassium [K^+]) and strong acid anions (eg chlorine [Cl^-], sulfate [SO_4^{2-}]) that is created during the chemical weathering of minerals. These equations and associated thermodynamic constants have been thoroughly studied (Dickson *et al.* 2007).

Concentrations of dissolved "free" CO_2 are often reported in terms of partial pressure, pCO_2, which is the equivalent atmospheric CO_2 concentration that would be in equilibrium with the water sample. Typical pCO_2 units are parts per million (ppm) volume of CO_2 per volume of air, or microatmospheres (μatm). Thus, pCO_2 does not directly refer to a concentration of free CO_2 in water but rather the result of the application of Henry's Law of gas dissolution equilibrium, which simply states that at a given temperature the concentration of a dissolved gas is proportional to the partial pressure of that gas in equilibrium with the solution.

C balances. Furthermore, recent re-evaluations of the factors used to generate regional CO_2 outgassing estimates – pCO_2 concentrations, k, and areal extent of inundation – along with a more balanced consideration of the tropics and wetlands all support an increase to published values for regional and global CO_2 outgassing fluxes (Table 1 and WebPanel 1). Such estimates would have direct consequences on net C balances on land because of the need to balance global, regional, and even local C budgets.

The effort to quantify the net C sink in mature rainforests in the Amazon Basin is an excellent case study, demonstrating the importance of rivers in coupling terrestrial and atmospheric C cycles (Richey *et al.* 2002; Ometto *et al.* 2005). Net ecosystem exchange (NEE; Panel 1) of C – measured by eddy covariance flux towers situated throughout the Amazon Basin – has ranged from high forest sinks to modest sources (–6 to +1 megagrams [Mg] C ha^{-1} yr^{-1}; Ometto *et al.* 2005), yet biomass and soil surveys generally yield lower sink estimates (Ometto *et al.* 2005; Chave *et al.* 2008). Richey *et al.* (2002) suggested that lateral C exports to streams could play a potential role in balancing this discrepancy. In response, two studies examined whether lateral stream exports might be important relative to terrestrial fluxes (Waterloo *et al.* 2006; Johnson *et al.* 2008). For streams in the seasonally dry southern Amazon, a net export of 0.40 Mg C ha^{-1} yr^{-1} was calculated (Johnson *et al.* 2008) for dissolved CO_2, which is largely outgassed within the few hundred meters downstream of groundwater seeps or springs, representing one-half of total deep-soil respiration; Johnson *et al.* (2008) also estimated that an additional 0.10 Mg C ha^{-1}

yr^{-1} was exported as dissolved organic carbon (DOC). Because no eddy covariance tower was present at the sites studied by Johnson *et al.* (2008), comparisons with published Amazon NEE values from other sites led us to estimate that stream export of groundwater CO_2 and DOC could account for 10–100% of NEE at that site (Ometto *et al.* 2005; Johnson *et al.* 2008). Waterloo *et al.* (2006) measured DOC and particulate organic carbon (POC) exports in a 2nd- to 3rd-order blackwater stream within an eddy covariance tower site, and estimated 0.19 Mg C ha^{-1} yr^{-1} of OC export to represent 5–6% of NEE. This estimate does not include dissolved CO_2, yet our few measurements of CO_2 degassing from these highly acidic streams immediately upstream of Waterloo *et al.*'s (2006) OC monitoring site are as high as, or even higher than, those of Johnson *et al.* (2008), suggesting that >15% of NEE may be exported as dissolved CO_2 and OC (Aufdenkampe unpublished). Neither study was able to compare local NEE measurements with the full suite of stream C exports, including DOC, POC, and total dissolved inorganic carbon (DIC, which includes CO_2; Panel 2). Nevertheless, in a peatland system in Scotland, Billett *et al.* (2004) were able to account for all lateral C exports via streams within the footprint of an eddy covariance tower and demonstrated that NEE changed from a net sink of 0.278 Mg C ha^{-1} yr^{-1} to a net source of 0.083 Mg C ha^{-1} yr^{-1} when lateral stream fluxes were considered. One challenge, however, of comparing stream C exports with NEE is whether the evaded CO_2 (from groundwater or respired from organic matter) is already captured within the footprint of the eddy covariance tower. Regardless, these studies suggest that lateral transport of C by streams should be considered when evaluating net ecosystem carbon balance (Chapin *et al.* 2006).

■ Carbon sequestration from soils to sea: erosion is key

Geologists and oceanographers have long hypothesized that there is a connection between tectonic uplift, mineral erosion, C burial, and atmospheric oxygen over geological time scales (Berner 1989), with river systems implicitly coupling the biogeochemical cycles between continents, oceans, and atmosphere. Studies of OC turnover in soils and sediments have begun to describe the mechanisms for the coupling of mineral and biogeochemical cycles via organo-mineral complexation, which is a critical factor in stabilizing OC (Hedges and Keil 1995). Yet OC and mineral production are typically spatially separated. Biological

S

Sulfur

32.065

primary production mainly occurs where there is light – that is, above the soil surface or in the low-turbidity euphotic zone of lakes and oceans. Mineral surfaces are produced at the bedrock–soil interface and subsoil, where primary minerals are chemically weathered to secondary alumino-silicate clays and iron and aluminum hydroxides. In most systems, the flux of OC mobilized into river corridors and the coastal oceans is substantially greater than the system's capacity to stabilize it via organo-mineral complexation, burial into anoxic environments, or other mechanisms. Thus, most OC is rapidly metabolized or photolysed and returned to the atmosphere as CO_2 (Cole *et al.* 2007). Therefore, the rate of erosion, delivery, and mixing of fresh mineral surfaces with fresh organic matter could likely control watershed- to global-scale C sequestration fluxes over both current and geological time scales (Hedges 2002; Kennedy *et al.* 2006).

A series of reports and letters responding to Van Oost *et al.* (2007) serves to highlight an ongoing debate over whether anthropogenic erosion might result in a globally important C sink (Stallard 1998), an important net CO_2 source (Lal 2003), or a combination that yields a slight net sink (Van Oost *et al.* 2007). Previous studies have explicitly considered one or more of three mechanisms linking erosion–deposition processes to alterations of net CO_2 fluxes between the land and the atmosphere: (1) complete to partial replacement of soil OC at eroding agricultural sites via crop production (Stallard 1998); (2) burial and inhibited decomposition of OC eroded from topsoils

(Stallard 1998); and (3) enhanced decomposition of soil OC due to the breakdown of protective soil structures during erosion and transport (Lal 2003). Nevertheless, these studies did not consider a fourth mechanism that could substantially augment estimates of global C sequestration due to erosion: (4) the transport of OC-poor minerals from deep soil horizons into environments where stable C-mineral complexes are formed with otherwise fresh, reactive C (Aufdenkampe *et al.* unpublished).

The conventional scientific perspective is that, globally, rivers discharge about 0.4 Pg C yr^{-1} as OC to the oceans, with about one-half in the form of DOC and one-half as POC, and an additional 0.5 to 0.4 Pg C yr^{-1} as DIC (Schlünz and Schneider 2000; Figure 3). These estimates have changed surprisingly little over time, despite revisions to both sediment delivery fluxes and the concentrations of POC associated with those sediments (Berner 1989; Schlünz and Schneider 2000). Geomorphologists have known, however, that only 5–25% of eroded sediment actually reaches the oceans, with most being deposited at the bottom of hillslopes (ie colluvium), in floodplains and wetlands (ie alluvium), and in reservoirs, lakes, and estuaries (Figure 4). This is apparent when comparing recent global estimates of modern fluxes of 12.6 Pg yr^{-1} of sediment delivered to the oceans (Syvitski *et al.* 2005) with estimates of modern erosion fluxes of 50–150 Pg yr^{-1} of soil (Stallard 1998; Wilkinson and McElroy 2007). Conservatively assuming that the OC content of these sediments averages 1%, then about

Table 1. Estimates of CO$_2$ outgassing from inland waters, for zones based on atmospheric circulation

Zone-class	Area of inland waters (1000s km^2)	pCO$_2$ (ppm)	Gas exchange velocity (k$_{600}$, cm hr^{-1})	Areal outgassing (g C m^{-2} yr^{-1})	Zonal outgassing (Pg C yr^{-1})
	min–max	median	median	median	median
Tropical (0°– 25°)					
Lakes and reservoirs	1840–1840	1900	4.0	240	0.45
Rivers (>60–100 m wide)	146–146	3600	12.3	1600	0.23
Streams (<60–100 m wide)	60–60	4300	17.2	2720	0.16
Wetlands	3080–6170	2900	2.4	240	1.12
Temperate (25°–50°)					
Lakes and reservoirs	880–1050	900	4.0	80	0.08
Rivers (>60–100 m wide)	70–84	3200	6.0	720	0.05
Streams (<60–100 m wide)	29–34	3500	20.2	2630	0.08
Wetlands	880–3530	2500	2.4	210	0.47
Boreal and Arctic (50°–90°)					
Lakes and reservoirs	80–1650	1100	4.0	130	0.11
Rivers (>60–100 m wide)	7–131	1300	6.0	260	0.02
Streams (<60–100 m wide)	3–54	1300	13.1	560	0.02
Wetlands	280–5520	2000	2.4	170	0.49
Global		Percent of global land area			
Lakes and reservoirs	2800–4540	2.1%–3.4%			0.64
Rivers (>60–100 m wide)	220–360	0.2%–0.3%			0.30
Streams (<60–100 m wide)	90–150	0.1%–0.1%			0.26
Wetlands	4240–15 220	3.2%–11.4%			2.08
All inland waters	**7350–20 260**	**5.5%–15.2%**			**3.28**

Notes: see WebPanel 1 for associated references.

N

Nitrogen

14.007

Figure 4. A typical floodplain deposit exposed at a cutbank on the Ucayali River, which drains the Peruvian Andes to form the Amazon River. Depositional events can lay down 20 to ≥100 cm of sediment in a few days, burying a forest floor that may have developed over decades, as shown here. Average annual deposition rates for these floodplains can exceed 5 cm yr^{-1} (Aalto et al. 2003). Such dynamic floodplain environments are common around the world in foreland basins, which are mid-continent depressions that continuously generate sediment accommodation space as uplifting mountain belts depress adjacent continental plates.

0.5–1.5 Pg C yr^{-1} is buried with those sediments in continental settings before reaching the oceans. These values match the 0.6–1.6 Pg C yr^{-1} that Stallard (1998) estimated is buried as a result of anthropogenic erosion alone. The low end of these values matches the 0.6 Pg C yr^{-1} burial flux for lakes and impoundments that Tranvik *et al.* (2009) estimated from extrapolating areal C burial fluxes (Figure 3). However, Tranvik *et al.* (2009) did not consider floodplains, wetlands, or colluvium.

Multiple lines of evidence (described above) suggest that an order of magnitude more C is buried annually in stable continental deposits than is buried within sediments in the world's oceans, and most of this C burial on continents is driven by human-induced erosion (Stallard 1998; Wilkinson and McElroy 2007). Critically, these C fluxes – which are substantial relative to global and regional net terrestrial ecosystem C balance – are sensitive to future climate and land-use change.

■ Mineral weathering and the coastal buffering system: can human activities on continents affect coastal acidification?

Rising atmospheric CO_2 and other global changes are altering the acid/base chemistry and carbonate buffering system of estuaries and coastal systems (Andersson *et al.* 2005; Doney *et al.* 2009). As for the open ocean, rising atmospheric CO_2 due to human activities increases seawater pCO_2 concentrations by air–water gas exchange. The additional dissolved CO_2 combines with water to form carbonic

acid (H_2CO_3), which can then dissociate into bicarbonate (HCO_3^-) and hydrogen (H^+) ions, the latter leading to a reduction in pH (Panel 2). The resulting suite of chemical changes – often termed ocean acidification – also includes a reduction in the carbonate ion (CO_3^{2-}) concentration, which tends to increase the solubility of calcium-carbonate ($CaCO_3$) minerals such as aragonite and calcite, which are used by many organisms to build shells and skeletons.

The acid/base chemistry of estuaries and coastal ecosystems is particularly susceptible to global change because of additional water, solute, and sediment inputs from the continents and because the buffering capacities in such ecosystems are typically lower than those in the open ocean. Processes such as riverine freshwater inputs, acid rain, atmospheric dry deposition, sediment denitrification, anaerobic organic matter decomposition, and submarine groundwater discharge all have large impacts on the coastal inorganic C system (Doney *et al.* 2007; Fennel *et al.* 2008; Thomas *et al.* 2009; Borges and Gypens 2010). Most of these processes are susceptible to anthropogenic forcing, and coastal ecosystems are particularly sensitive to higher pCO_2. Seagrasses and some types of phytoplankton exhibit higher rates of photosynthesis under elevated aqueous CO_2, and other organisms may be sensitive to altered pH, particularly at the larval and juvenile stages (Waldbusser *et al.* 2010). Measuring and assessing these changes in water chemistry is difficult, however, because of the dynamic nature of coastal systems and the limited historical observations that are available for many locations. Estuarine and coastal waters often feature substantial spatial and temporal variability in pH and CO_2 due to physical processes (eg tides, mixing, turbulence, currents) and biogeochemical C metabolism (eg photosynthesis, respiration, calcification, dissolution).

Changes in riverine chemistry and discharge often play a larger role than local processes in most estuarine and many other coastal systems, and can either offset or accelerate coastal acidification. Enhanced delivery of watershed nutrients and the resulting eutrophication can alter coastal CO_2 concentrations (Borges and Gypens 2010). Agricultural (Oh and Raymond 2006), mining (Brake *et al.* 2001; Raymond and Oh 2009), and urban/suburban practices (Barnes and Raymond 2009) have been linked to direct changes in the delivery of buffering capacity to streams and rivers. These changes have the potential to alter the concentrations of inorganic C species expected through mixing of fresh water and seawater.
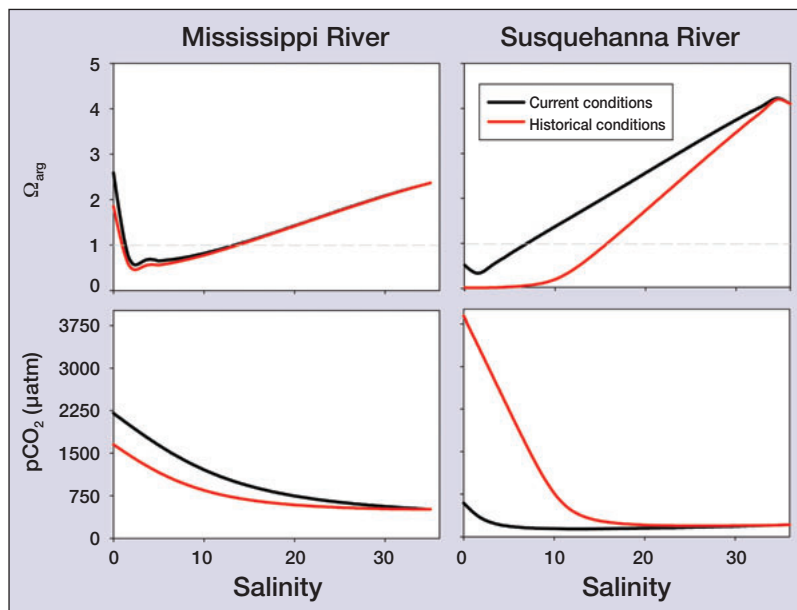
In North America, the Mississippi and Susquehanna rivers have both experienced large changes in carbonate alkalinity (Carb$_{alk}$ = [HCO_3^-] + 2×[CO_3^{2-}]; Panel 2) concentrations over the past century (Raymond *et al.* 2008; Raymond and Oh 2009). These two rivers and their estuaries offer an example of how differences in the chemistry and anthropogenic pressures of watersheds can lead to contrasting coastal ocean responses (Figure 5). The Mississippi River has experienced a 25% increase in Carb$_{alk}$ over the past 60 years, accompanied by no change

in pH; this has resulted in a potential modest increase in both pCO_2 and aragonite saturation state (Ω_{arg}) in adjacent coastal waters (Ω_{arg} is the stability of aragonite mineral, where $\Omega_{arg} < 1$ indicates that the solution is undersaturated and dissolution can occur; Figure 5). The combination of stable pH and increasing pCO_2 are likely due to greater respiration of OC to CO_2 within river waters, which may indicate that inputs of labile OC are now also higher upstream as a result of eutrophication. Increasing Ω_{arg} reflects decreasing solubility, and a value of 1 marks the threshold between unsaturated and saturated conditions. In contrast, the Susquehanna River was acidic during the early 1940s on account of discharges from local mining operations, with a theoretical $\Omega_{arg} < 1$ throughout most of Chesapeake Bay to which it drains, which has a salinity below 15 parts per thousand during much of the year (Pritchard 1952; Figure 5). With the abandonment of mining in the watershed, Ω_{arg} of Chesapeake Bay has recovered, presumably close to pre-mining levels, and pCO_2 concentrations are now much lower than those observed historically.

With respect to future changes and other watersheds, how anthropogenic watershed disturbance alters the $CaCO_3$ saturation state and carbonate chemistry at a given salinity is dependent on the changes in the riverine fluxes of Ca^{2+}, $Carb_{alk}$, and DIC, as well as the initial ratios of $Carb_{alk}$:DIC and Ca^{2+}:CO_3^{2-}. Alterations in watershed hydrology are a primary determinant of these fluxes, and future changes are expected as a consequence of global warming. For instance, the Mississippi River now exports ~45% more $Carb_{alk}$ than it did historically, partly as a result of an acceleration of the hydrological cycle (Raymond *et al.* 2008), which currently offsets a portion of regional coastal acidification. Human land-use patterns are also substantially changing river loadings of nutrients, particulate and dissolved organic matter, and sediments, all of which will influence coastal ocean biogeochemistry. Interactions between river chemistry alterations, climate change, expansion of low-dissolved-oxygen zones, and ocean acidification are poorly defined, and the impact of these multiple stressors on coastal ecosystems is a major research challenge for the future (Doney 2010).

Conclusion

Terrestrial ecologists and global C modelers alike will benefit from considering the coupling of the Earth's systems by rivers and other inland waters. The old rule of thumb that "rivers export 1% of terrestrial GPP [gross primary production]" might well be replaced by a new one:

Figure 5. Calculated changes in the aragonite saturation state (Ω_{arg}) and pCO_2 for North America's Mississippi and Susquehanna rivers during estuarine mixing. Data for the Susquehanna River are taken from the US Geological Survey site 01570500 (1944–1995). We obtained annual average concentrations of alkalinity, calcium, and pH using Yale LoadRunner software (http://environment.yale.edu/loadrunner/). For the Mississippi River, we used $Carb_{alk}$ concentrations from Raymond et al. (2008); we assumed a 40 micromolar (μM) increase in calcium and no change in pH. For both the Mississippi and Susquehanna rivers, we calculated concentrations of carbonate and pCO_2 using reported pH ocean values (Bates and Hansell 1999; Cai 2003).

"rivers receive, transport, and process the equivalent of terrestrial NEP in their watersheds".

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30.974

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S

Sulfur

32.065

WebPanel 1. Re-evaluation of global CO_2 fluxes from inland waters

Published estimates of the global flux of carbon dioxide (CO_2) outgassing from inland surface waters have been calculated via averages of partial pressures of dissolved CO_2 (pCO_2) concentrations, gas exchange velocities (k), and areal extent of inundation that are biased toward northern latitudes (Cole and Caraco 2001; Cole *et al.* 2007; Battin *et al.* 2009; Tranvik *et al.* 2009). Recent re-evaluations of temperature dependencies of these factors and more balanced consideration of the tropics and of wetlands all contribute to a need to further increase estimates of regional and global CO_2 outgassing fluxes. Here we discuss each of these factors, and provide support for our revised global CO_2 outgassing estimates provided in Table 1.

Partial pressures of dissolved CO_2 are a function of organic carbon mineralization fluxes minus outgassing fluxes from the water surface (see supplementary discussion in Mayorga *et al.* 2005). Two studies have shown that pCO_2 has a strong positive relationship with water temperature (Marotta *et al.* 2009; Kosten *et al.* 2010), reflecting the temperature dependence of respiration. The slopes of these published log-linear relationships show a 2x to 3x increase in pCO_2 for a 10˚C increase and a 4x to 7x increase in pCO_2 for a 20˚C increase. In addition, many published pCO_2 values may include underestimates because of inattention to gas evasion during sample handling, which can be rapid and substantial, before a pH, pCO_2, or dissolved inorganic carbon measurement. In Table 1, we present median pCO_2 values for each climate zone and inland water type, based on a synthesis of thousands of data points from our own measurements and data available in the literature (Alin *et al.* unpublished; Cole and Caraco 2001; Richey *et al.* 2002; Mayorga *et al.* 2005; Johnson *et al.* 2008; Marotta *et al.* 2009; Humborg *et al.* 2010).

To translate water–air CO_2 gradients to areal fluxes requires multiplication by k, which varies as a function of turbulence in the surface water and, to a lesser degree, temperature. Gas exchange velocities can be challenging to measure, and published values for CO_2 exchange velocities for streams and rivers are sparse. The few syntheses of global CO_2 evasion fluxes from fresh waters have used conservative k values of 2 to 4 cm hr^{-1} obtained from studies of lakes, where wind is often assumed to be the primary driver of surface turbulence (Cole and Caraco 2001; Cole *et al.* 2007; Table 1). Turbulence in streams and rivers is increased by flow over rough elements in channel bottoms (ie boulders, sand bars), and direct measurements of CO_2 exchange velocities in flowing waters range from 3 to 30 cm hr^{-1} (Raymond and Cole 2001; Bott *et al.* 2006; Table 1). Previous global CO_2 evasion estimates have not considered the effect of temperature on k and have implicitly assumed uniform global water temperatures similar to those in the temperate zones. For water with the same surface turbulence, a 10˚C increase translates to a 30–37% increase in k and a 20˚C increase to a 70–79% increase in k. Considering both the increased turbulence of streams and rivers and the temperature effects on k requires that we further upwardly revise current estimates of water-to-air CO_2 fluxes from inland waters. In Table 1, we present median k_{600} values – the CO_2 gas transfer velocity normalized to 20˚C in freshwater, which has a Schmidt number of 600 – for each climate zone and inland water type based on a synthesis of data from our own measurements and data available in the literature.

Remote-sensing approaches can quantify actual inundated area as a function of time (Hess *et al.* 2003; Prigent *et al.* 2007), to which areal outgassing fluxes can be directly applied for estimating spatial and temporal patterns of CO_2 gas evasion from inland waters. In Table 1, we summarize seasonally maximum inundated areas by grouping the 12 classes quantified by Lehner and Döll (2004) – each multiplied by empirically derived "undersampling factors" of 1.73, 1.22, and 1.56 for lakes, reservoirs, and wetlands, respectively – as developed by Downing (2009) to include inland waters smaller than the 60- to 100-m resolution of Lehner and Döll's (2004) analysis. We present the area of the large rivers class (>60–100 m width), as calculated by Lehner and Döll (2004), then estimate the small rivers and streams class (<60–100 m width) using Downing's (2009) empirically derived undersampling factor of 1.41. In Table 1, we calculate seasonally minimum inundated areas by multiplying maximum areas by the minimum-to-maximum inundation ratios developed by Prigent *et al.* (2007) for each zone, in order to account for dry season wetland retreat and cold season freezing.

Different inland water types in different climates each have characteristically different pCO_2, k_{600}, and areal gas evasion values (Table 1), with consequences to globally integrated fluxes. For example, small rivers and streams have a disproportionate global flux due to their high k_{600} values and the tropics have a disproportionate global flux due to high pCO_2 values and to higher k values after temperature corrections (Table 1). Wetlands are a particularly diverse class, with large seasonal variations in inundation. They include floodplains, swamp forests, coastal marshes, bogs, intermittent lakes, and patchy wetland complexes. Because of this complexity and seasonality, Cole *et al.* (2007) explicitly excluded wetlands from their global synthesis. We have included wetlands because most wetlands: (1) receive inputs from upland terrestrial ecosystems; (2) are hydrologically connected to downstream waters; (3) process carbon differently from upland ecosystems; (4) are highly susceptible to climate and land-use change; and (5) are not included in terrestrial carbon budgets.

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